

FUNCTIONAL MOLECULAR GROUPS ON INTERSTELLAR GRAINS

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ABSTRACT

Chemical routes in the synthesis of large interstellar molecules are quite obscure, but interstellar grains are believed to play a significant role. We suggest that functional molecular groups (e.g., OH, CH, CH₂, CH₃, NH₂, etc.) on grain surfaces may provide the precursor basis for ensuing grain chemistries that produce complex molecules. Herein we report a first attempt to determine the relative abundance ratios of molecular groups toward the Galactic center and the Orion Nebula by using previously reported gas-phase abundances of complex molecules observed with single antennas having arcminute resolutions. Specifically, for SgrB2(OH), which is an extended cloud possessing no concentrated molecular core, we obtain OH:CH₃:CH₂:CH:NH₂:HCO:CN ~ 4190:100:29:71:36:57:178, and for OMC-1 we obtain OH:CH₃:CH:NH₂:HCO ~ [4040–8080]:100:36:25:[83–167], where both sets of relative abundances are normalized to the CH₃ group. We suggest that these ratios may represent the relative abundance of the functional molecular groups on grain surfaces where the molecules were formed and subsequently released into the gas phase. We find that the relative functional group ratios in SgrB2 and OMC-1 are similar based on single-antenna beam-averaged abundances. We predict that higher spatial resolution (i.e., better beam-source coupling, as afforded by interferometric arrays) should be able to establish the role of functional molecular groups on grain surfaces in more compact interstellar molecular environments possessing a variety of different physical conditions.

Subject headings: ISM: abundances — ISM: clouds — ISM: molecules — molecular processes

1. INTRODUCTION

Molecular synthesis of complex molecules that tend toward saturation (hydrogen-rich) cannot be explained by gas-phase chemistry alone. For example, ethanol and dimethyl ether abundances are observed to be at least an order of magnitude larger than abundances estimated by gas-phase chemistry (Millar et al. 1988). Similarly, the fractional abundance of ammonia from hot, dense regions is approximately 2 orders of magnitude larger than that observed in cold, dark clouds. This is believed to be due to the evaporation of ammonia ice from the surface of interstellar grains (Pauls et al. 1983). A similar explanation is offered for the enhanced abundance of methanol (Menten et al. 1986) and deuterated water (Olofsson 1984; Moore, Langer, & Huguenin 1986; Henkel et al. 1987) in hot cores associated with young stellar objects. Hence, interstellar grain surface chemistry, which does adequately explain the formation of simple molecular hydrogen (see Duley & Williams 1984), probably also makes important contributions to the formation of the larger molecular species (i.e., species containing five atoms or more). However, grain chemistry is poorly understood with respect to heavy molecule synthesis since the composition, charge, and chemical nature of the grains themselves are not known.

The prevailing current grain chemistry models are thermal; that is, the grains are assumed to be at a constant low temperature. Under this condition, only very light species, such as atoms (particularly H, but also C, N, and O), move very much on the grain surfaces. Thus, reactions are dominated by atom-atom and atom-molecule encounters rather than by molecule-molecule collisions. For example, surface methanol could be made by successive

hydrogenation of CO by H atoms. Other heavy molecular species might then be made in the gas phase by ion-molecule reactions from surface-released methanol, but it is not known exactly how this would be accomplished.

Another view of grain chemistry posits that thermal spikes occur, during which time simple species on the grain are free to move around on the surface to form more complex species, but this synthesis avenue requires small grains to be transiently heated by UV photons in dark cloud regions where such photons are believed to be very rare. Additionally, thermal spikes would also require a non-thermal analysis of grains, making the problem more complicated and more uncertain.

The standard grain chemistry model, in which more mobile H atoms dominate surface reactions, producing mainly small saturated species (e.g., CH₄, NH₃, H₂O), need not be correct. For example, new experimental results of Katz et al. (1999) show that H atoms diffuse more slowly than anticipated by astrochemists. Moreover, if grain surface chemistries produce all of the large molecular species, modifications induced by subsequent gas-phase chemistry may not be particularly extreme. If the aforementioned conditions prevail, we suggest that functional molecular groups (e.g., OH, CH, CH₂, CH₃, NH₂, etc.) on grain surfaces may provide the precursor basis for ensuing grain chemistries. This approach assumes that H atom reactions are sufficiently slow that heavy atoms can combine on grains, thereby permitting a wide variety of functional molecular groups to form at grain sites. Each such surface group would be subject to the following scenarios: (1) the group could undergo successive hydrogenation as in the prevailing grain chemistry thermal model, (2) the group could react with gaseous species that impinge on the grains, or (3) the group could diffuse over the grain surface and react with another surface group under favorable conditions such as a thermal transient, reduction of H atom surface reactions, or reduction of H atom surface abun-

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dance, as postulated by Brown (1990). Subsequently, stable heavy molecular species could be formed by combinations of the above scenarios. No matter how the final stable species are formed, observations would point to the precursor functional molecular groups on the grains from which such species originate. Moreover, such a grain chemistry scenario could account for the high degree of isomerism seen in interstellar clouds (Hollis, Lovas, & Jewell 2000). For example, at present there are approximately 92 polyatomic molecules detected in interstellar clouds, and 22 of these species are associated with eight isomeric pairs (e.g., dimethyl ether and ethanol) or two isomeric triplets (i.e., acetic acid, methyl formate, and glycolaldehyde).

Given that functional molecular groups on grains may be involved in the synthesis of heavy molecular species, we undertook a comparative study of heavy gas-phase interstellar molecular abundances to determine molecular group abundance ratios for the Galactic center and the Orion Nebula. Our primary hypothesis is that forming the abundance ratio from a judicious choice of two different molecular species (i.e., each containing common functional group[s]) would result in the abundance ratio of the functional groups not common to both molecular species. For example, forming the ratio of the abundances of methanol ($\text{CH}_3\text{-OH}$) and methylamine ($\text{CH}_3\text{-NH}_2$) would result in the abundance ratio $\text{OH}:\text{NH}_2$. This technique is analogous to forming the ratio of the abundances of two isotopic forms of a particular molecule to obtain the ratio of the two isotopes; such isotopic ratios are routinely used to compare one source with another in order to determine differences in the chemistry that occurred (e.g., stellar processing and/or chemical fractionation). Similarly, group ratios are dependent upon the relative chemistry that occurs between species within a given source. For example, all the effects that determine the chemistries within a given source (e.g., species formation and loss mechanisms, associated rates, etc.) should be inherent in the group ratios, which may be useful diagnostics if systematic patterns emerge.

2. THE DATA

For the methodology advocated here, an optimal source comparison would be achieved if one could observe a large ensemble of heavy molecules in sources where the telescope beam couples well to those sources. Unfortunately, the present state of affairs is that only a few large molecules have been systematically studied with millimeter-wave arrays, which afford the best beam coupling with more compact sources. Thus, for our initial effort here, we are restricted to millimeter-wave surveys conducted with single antennas of ensembles of heavy molecules that have been observed in large inhomogeneous sources comprised of extended structures and compact cores having a variety of physical conditions.

One of the most notable and extensive of these single-antenna surveys is that reported by Turner (1989), who conducted a molecular line survey of OMC-1 and SgrB2(OH) from 70 to 115 GHz with the NRAO³ 11 m telescope. The 11 m telescope half-power beamwidth changes from $\sim 100''$ to $\sim 60''$ as frequency changes from 70 GHz to 115 GHz, respectively. Thus, in the case of both sources and particu-

larly at the lower frequencies, the telescope beam samples a number of distinct features in each source. For example, in the direction of OMC-1 the "source" is comprised of a number of different components of varying temperatures, velocities, and sizes (e.g., the hot core, the compact ridge, the plateau source near IRc2, and the extended cloud), and all components lie within the telescope beam. Similarly, in the direction of SgrB2(OH), which is extended and contains no prominent molecular core, there are also dense star-forming cores to the north, such as SgrB2(M) ~ 0.5 away and SgrB2(N) ~ 1.5 away. In any case, the data stemming from the Turner (1989) survey samples two vastly different regions of the Galaxy with the same telescope beam—the Galactic center lying 8.5 kpc away and the nearby Orion Nebula lying 450 pc away. Although different volumes are included in the beam at the distances of Orion and SgrB2, the relative abundances within a given source are averaged over the same volume. Thus, comparison of these global average abundances is probably valid. If so, then we suggest that differences in their relative abundances may reflect differences in the abundances of the molecular groups of which they are composed.

Turner (1991) calculated total column density abundances for all the species detected in the Turner (1989) survey. We will base most of our analysis on the Turner (1991) results except for the abundance determination of methyl formate relative to the abundance of dimethyl ether toward OMC-1; this particular abundance ratio is not consistent with OMC-1 surveys of other investigators (e.g., see Johansson et al. 1984; Blake et al. 1987; Sutton et al. 1995; and Schilke et al. 1997).

3. RESULTS AND DISCUSSION

Large molecules can be broken down into their constituent molecular groups. In this sense, molecular groups are the building blocks of heavy molecules believed to be synthesized on the surface of interstellar grains, or, alternatively, synthesized by a combination of grain and gas-phase chemistry in hot core regions (e.g., Charnley et al. 1995). Table 1 shows the molecular group ratios calculated for SgrB2(OH) and OMC-1 from abundance determinations for the molecular species involved. Note that on each row, a pair of heavy molecular species has been chosen to have one or more structural groups in common, thereby permitting a determination of the molecular group ratio claimed for that row. For example, consider the entry for methanol ($\text{CH}_3\text{-OH}$) and methylamine ($\text{CH}_3\text{-NH}_2$). Since both have the CH_3 group in common, the abundance ratio of methanol and methylamine should give the abundance ratio $\text{OH}:\text{NH}_2$.

Table 1 largely exploits the molecular group ratios possible in the Turner (1991) data. Note from Table 1 that the group ratio $\text{CH}_3:\text{HCO}$ has been independently determined twice in SgrB2(OH), and the values agree to better than a factor of 2. This suggests that the relative abundances of the functional groups may be independent of the particular carrier molecules in a given source. For each molecule used in Table 1, we used the abundance determinations for which Turner (1991) excluded anomalous transitions that are obviously not in LTE or are plagued by optical depth effects (e.g., all transitions of CH_3CN). We chose those abundance determinations that included all available valid data, and summed any multicomponent abundances to obtain a global result for the source. In this way, we

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Table 1
MOLECULAR GROUP ABUNDANCE RATIOS FROM GAS-PHASE MOLECULE ABUNDANCES

Group Ratio ^a	Ratio Determined from Heavy Molecule ^b Pairs	SgrB2(OH)	OMC-1
OH:NH ₂	CH ₃ OH, CH ₃ NH ₂	125.0	...
OH:HCO	CH ₃ OH, HCOCH ₃	68.2	48.5
OH:CN	CH ₃ CH ₂ OH, CH ₃ CH ₂ CN	23.6	...
CH ₃ :NH ₂	HCOCH ₃ , HCONH ₂	2.5	4.0
CH ₃ :HCO	CH ₃ OCH ₃ , HCOOCH ₃	2.1	0.6–1.2 ^c
CH ₃ :HCO	CH ₃ NH ₂ , HCONH ₂	1.4	...
CH ₃ :CH	CH ₃ CH ₂ CN, CH ₂ CHCN	1.4	2.8
CH ₂ :NH ₂	CH ₂ CN, NH ₂ CN	0.8	...
HCO:NH ₂	HCOCH ₃ , CH ₃ NH ₂	1.8	...

^a All group ratios were calculated from Turner (1991) abundance determinations unless otherwise stated.

^b Heavy molecule formulae have been written for structural group clarity. That is, acetaldehyde is usually written CH₃CHO but we have used HCOCH₃, and formamide is usually written NH₂CHO but we have used HCONH₂.

^c This CH₃OCH₃ and HCOOCH₃ group ratio range was calculated from abundance determinations in OMC-1 surveys by Johansson et al. (1984), Blake et al. (1987), Sutton et al. (1995), and Schilke et al. (1997; see text).

expected to test the relative global chemistries toward SgrB2(OH) and OMC-1 with the relatively extensive set of abundance determinations of Turner (1991). Only in one instance in OMC-1 were we compelled to use abundance determinations of other investigators rather than those of Turner (1991): the OMC-1, CH₃OCH₃, and HCOOCH₃ abundance determinations from Turner (1991) yield CH₃:HCO ~ 0.2, which is not consistent with other investigations, presumably because of a two-component fit assumption that Turner (1991) used for the HCOOCH₃ data. Thus, in Table 1 we used CH₃OCH₃ and HCOOCH₃ abundance determinations from other OMC-1 surveys (e.g., Johansson et al. 1984; Blake et al. 1987; Sutton et al. 1995; and Schilke et al. 1997) to estimate a range for CH₃:HCO.

From Table 1 we find that the relative abundances for groups in SgrB2(OH) are

$$\text{OH:CH}_3\text{:CH}_2\text{:CH:NH}_2\text{:HCO:CN} \sim 4190:100:29:71:36:57:178, \quad (1)$$

where all data were normalized to the CH₃ group, which has been arbitrarily set to a value of 100. Similarly, for OMC-1, we obtained the following relative abundances:

$$\text{OH:CH}_3\text{:CH:NH}_2\text{:HCO} \sim [4040-8080]:100:36:25:[83-167]. \quad (2)$$

Note that the CH₂ group could not be included in the OMC-1 analysis, since CH₂CN and NH₂CN were not detected. Similarly, the CN group could not be included because the ratio of ethyl cyanide (CH₃CH₂CN) to ethanol (CH₃CH₂OH) is not reliable for OMC-1; the Turner (1991) ethanol abundance is based on extremely weak lines and is highly overestimated relative to dimethyl ether (CH₃OCH₃), as determined by both Sutton et al. (1995) and Schilke et al. (1997). If one considers ordering of the functional groups from most to least abundant, the two sources as expressed by relationships (1) and (2) would have nearly the same ordering. However, the important diagnostic is the magnitude of the functional group ratios involved.

Relationships (1) and (2) suggest that these two important molecular cloud sources have nearly similar chemistries. This may be due to the large sample volume resulting from

the single-antenna beam-averaged surveys used here. However, discrete components within OMC-1 may tend to be more oxide- or silicate-rich grain sources and could account for the greater number of carbon-bearing molecular species seen toward SgrB2(N), a hot, compact component north of SgrB2(OH). For example, on the surface of oxide or silicate grains a preponderance of the OH group is expected, while on the surface of carbon grains, groups like CH₃, CH₂, and CH would dominate (Duley & Williams 1984, p. 128). Alternatively, if large molecules are formed primarily as a result of modifications induced by gas-phase chemistry in hot cores, another interpretation due to differences in chemistries would be possible. For example, OMC-1 contains a hot core and compact ridge possessing large hydrogen-rich, N- and O-bearing molecules, respectively (Blake et al. 1987), but these species are apparently absent or not very abundant in the OMC-1 extended cloud (see Caselli, Hasegawa, & Herbst 1993). Thus, developing the relative abundance ratios of molecular groups for individual sources suggests a potential tool for intercomparing the nature of the grains and/or the gas-phase chemical alterations caused by environmental conditions.

While chemical routes in the synthesis of large interstellar molecules are not known, interstellar grains are believed to play a significant role as a surface repository for functional molecular groups, which are the building blocks of complex molecules containing at least five atoms and two or more molecular groups. Moreover, the grains, charged or neutral, may well act as chemically active or passive surfaces in some molecular synthesis reactions; but again, the exact chemical nature of the grains is uncertain. It is noteworthy that functional groups, such as the methyl radical (CH₃), the methylene radical (CH₂), and methylidyne (CH), have all been detected in interstellar clouds and are believed to populate diffuse clouds or extremities of dense clouds (see de Jong, Dalgarno, & Boland 1980; Hollis, Jewell, & Lovas 1995; Feuchtgruber et al. 2000). Presumably, these particular groups are locked up in more complex interstellar molecular species toward dense cloud cores, lending further support to a molecular formation scenario that would deplete these important functional groups where grains are most abundant. Theoretically, gas-phase chemistry in hot core regions can also account for the production of a

limited number of large molecular species such as alcohols (Charnley 1995), but this mechanism presently lacks observational confirmation (Snyder 2000, private communication).

4. SUMMARY

We have estimated the relative abundance ratios of molecular groups from previously reported molecular abundances of complex gas-phase molecules toward the Galactic center and the Orion Nebula. We suggest that these ratios may represent the relative abundance of the functional molecular groups on grain surfaces where the molecules were formed and subsequently released into the gas phase. Our study is limited to data obtained with single antennas that have beamwidths that encompass a range of different physical conditions within a given source. Thus, our global results for SgrB2(OH) and OMC-1 are similar, suggesting that the nature of interstellar grains and interstellar chemistries are similar in both sources when averaged over single-antenna resolutions. We advocate that more detailed studies of an ensemble of large molecules with an array be conducted on various compact sources and components (e.g., SgrB2[N], SgrB2[M], and the various components of OMC-1). Such detailed studies should be

able to determine the relative abundances of molecular groups toward compact sources where the interferometric beam can couple well to the source being investigated, thereby providing observational constraints on grain and/or gas-phase chemistry models in these sources. For example, if grain chemistry predominates, then a grain source rich in oxides or silicates would likely have a higher concentration of molecular groups containing oxygen, as compared with a source whose grains are more carbon-like. On the other hand, if large molecules are formed primarily as a result of modifications induced by gas-phase chemistry in hot cores, then the molecular group ratios would reflect the dominant temperature-dependent chemical pathways occurring in such sources.

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